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Tidiane Diop*, Libasse Diop, Kieran C. Molloy, Gabriele Kociok-Köhn and Djibril Fall

Synthesis, characterisation and crystal structure of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$

Abstract: The title compound, $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2 \cdot [(\text{PhPO}_3\text{H})_2\text{SnPh}_3]^-$, has been synthesised and its structure determined by spectroscopies (IR, RMN and Mössbauer) and single crystal X-ray crystallography. The Mössbauer spectroscopy data for the title compound ($Q_S = 3.50 \text{ mm s}^{-1}$) are in accordance with the $\text{trans-O}_2\text{SnC}_3$ geometry at tin atom. The SnPh_3 residue is axially coordinated by two monodentate $[\text{PhPO}_3\text{H}]^-$ anions, leading to a trigonal-bipyramidal geometry around the tin atom. The anions $[(\text{PhPO}_3\text{H})_2\text{SnPh}_3]^-$ are linked by pairs of O-H...O interaction, forming an infinite chain. In the crystal, neighbouring chains are linked by hydrogen bonds N-H...O via the cation $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2^+$, forming a three-dimensional network.

Keywords: bipyramidal trigonal; crystal structure; IR; Mössbauer; NMR; X-ray.

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Introduction

The interest to synthesise new organotin (IV) derivatives is related to their applications in different fields (agrochemicals, surface disinfectants and marine antifouling paints) (Evans et al., 1985; Weng et al. 1997; Basu et al., 2001; Gielen, 2002; Gielen et al., 2005; Davies et al., 2008) and explains the involvement of many groups in the search for new organotin compounds (Samuel et al., 2002; Chandrasekhar and Baskar, 2003; Nath et al., 2003). Our groups have so far published some articles dealing with

SnMe_3 and SnPh_3 residues containing derivatives with mono- and polybasic oxyanions (SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, PhPO_3H^- , HAsO_4^{2-} , ...) (Diassé-Sarr et al., 2004; Diop et al., 2011; Gueye et al., 2011; Sow et al., 2012). As a continuation of our research work for new organotin(IV) derivatives, we report here spectroscopic (IR, NMR, Mössbauer) and crystallographic studies of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$.

Results and discussion

In comparison to the data reported for other phenylphosphonate derivatives (Song et al., 2007; Chunlin et al., 2008; Shankar et al., 2011), we suggest the following assignments for the compound. The bands located at 1174 s, 1112 s, 1062 s cm^{-1} are assigned to the stretching vibrations of the PO_3 groups. The band at 506 cm^{-1} on the IR spectrum is assigned to δPO_3 . The ^{117}Sn resonance (-237 ppm) indicates the presence of the indiscernible trans-coordinated SnPh_3 residue in solution (Flinn et al., 1978). The Mössbauer spectra of the title complex show a slightly asymmetric quadrupole split doublet with an isomer shift value (1.24 mm^{-1}) in the normal range for the organotin(IV) derivative (Davies and Smith, 1982). The quadrupole splitting value (3.50 mm^{-1}) is consistent with trans-coordinated Ph_3Sn residues (Holecek et al., 1983). The di-isopropylammonium [bis(phenylphosphonato)triphenyltin(IV)] structure, is reported in Figure 1 with the numbering scheme. The structure of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$ consists of molecules in which two monodentate PhPO_3H^- bind a SnPh_3 moiety (Figure 1). The geometry around tin is trigonal bipyramidal with a $\text{trans-O}_2\text{SnC}_3$ stereochemistry, with the apical oxygen arising from the phenylphosphonato ligands. A similar chain arrangement around the tin atom has been observed in the crystal structure of catena-trimethyltin(IV) methylphosphonate (Diop et al., 2002). The sum of the angles of tin with the ipso-carbon atoms [$122.5^\circ(3)$, $110.5^\circ(5)$, $118.4^\circ(5)$] is 351.4° indicating significant deviation from planarity; the corresponding axial O(1)-Sn-O(4) is $178.1^\circ(3)$ and indicates a slight deviation from linearity. The two axial Sn-O distances are almost identical Sn-O(1) 2.194 (6) Å and Sn-O(2) 2.211(4) Å and are shorter than the Sn-O axial distances [2.240(6)

Å and 2.319(5) Å] observed in the α -(phenylphosphonato) trimethyltin(IV) reported by Molloy et al. (1981) and are longer than Sn-O axial distances [2.116(2) Å and 2.132(3) Å] observed in catena- $(\mu_2$ -phenylphosphinato O, O')-chloro-tin(II) (Adair et al., 2003). The geometry around the phosphorous atom in the ligands is a distorted tetrahedron (O(3)-P(1)-O(1) 114.7°(4) O(1)-P(1)-C(25) 112.6°(6) owing to steric hindrance. The hydrogen bonds O-H...O (2.567 Å) between type polymerises the mononuclear $[(\text{PhPO}_3\text{H})_2\text{SnPh}_3]^-$ and lead to an infinite chain (Figure 2). The crystal structure analyses of the title compound reveal the presence of dimeric symmetrical phosphoryl anion groups linked to each other via intermolecular O-H...O hydrogen bonds, [O-H 0.797 Å, H...O(3) 1.781 Å, O(3)...O(2) 2.567 Å] (Figure 2). In the crystal, neighbouring chains are linked via hydrogen bonds N-H...O interactions [N-H(0A) 1.481 Å, H(0A)...O(3) 1.901 Å, N(1)...O 2.790 Å] by the di-

isopropylammonium, generating a three-dimensional (3D) network (Figure 3). These hydrogen bonds contribute to the crystal stability and compactness and result in a 3D arrangement. The P-O(2)H distance is 1.572(9) Å similar to the same distance of 1.569(3) Å observed in $\text{Cy}_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnMe}_3$ (Diop et al., 2011).

Selected bonds (Å): Sn-C(13) 2.120(9); Sn-C(7) 2.125(9); Sn-C(19A) 2.150(9); Sn-C(19) 2.174(10); Sn-O(1) 2.194(6); Sn-O(4) 2.211(6); P(2)-C(31A) 1.757(15); P(2)-C(31) 1.856(14); N-C(4) 1.508(13); N-C(1) 1.541(12); P(1)-O(3) 1.509(7); P(1)-O(1) 1.514(6); P(1)-O(2) 1.572(9); P(1)-C(25) 1.699(10); P(1)-C(25A) 1.931(11); P(2)-O(4) 1.500(7); P(2)-O(5) 1.515(7); P(2)-O(6) 1.557(7).

Selected angles (°): C(13)-Sn-C(7) 122.5(3); C(7)-Sn-C(19A) 110.5(5); C(13)-Sn-C(19) 118.4(5); C(7)-Sn-C(19) 118.2(5); C(13)-Sn-O(1) 89.7(3); C(7)-Sn-O(1) 90.3(3); C(19A)-Sn-O(1) 89.0(5); C(19)-Sn-O(1) 99.5(5); C(13)-Sn-O(4) 89.0(3); C(7)-Sn-O(4) 89.2(3); C(19A)-Sn-O(4) 92.9(5); C(19)-Sn-O(4) 82.3(5); O(1)-Sn-O(4) 178.1(3).

Symmetry codes: (i) $-x+1/2, y-1/2, -z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$.

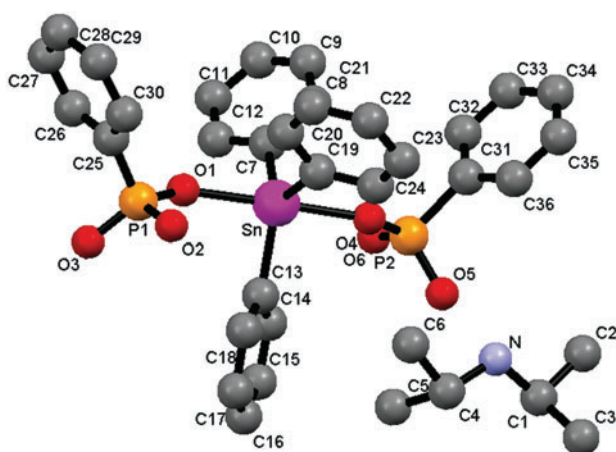


Figure 1 Asymmetric unit of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$ (H atoms are omitted for clarity).

Experimental

The infrared spectrum was recorded at the Laboratoire de Contrôle des Médicaments (UCAD, Dakar, Senegal) by means of a Bruker FT-IR type, the sample was prepared as a KBr pellet. Infrared data are given in cm^{-1} (abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad). Elemental analyses were performed at the University of Bath (UK) using an Exeter Analytical CE 440 analyser. Solution NMR spectra were recorded from a saturated CDCl_3 solution, at 250.27 and 89.27 MHz for ^1H and ^{117}Sn , respectively. ^1H and ^{117}Sn chemical shifts are given in ppm and are referred, respectively, to SiMe_4 and

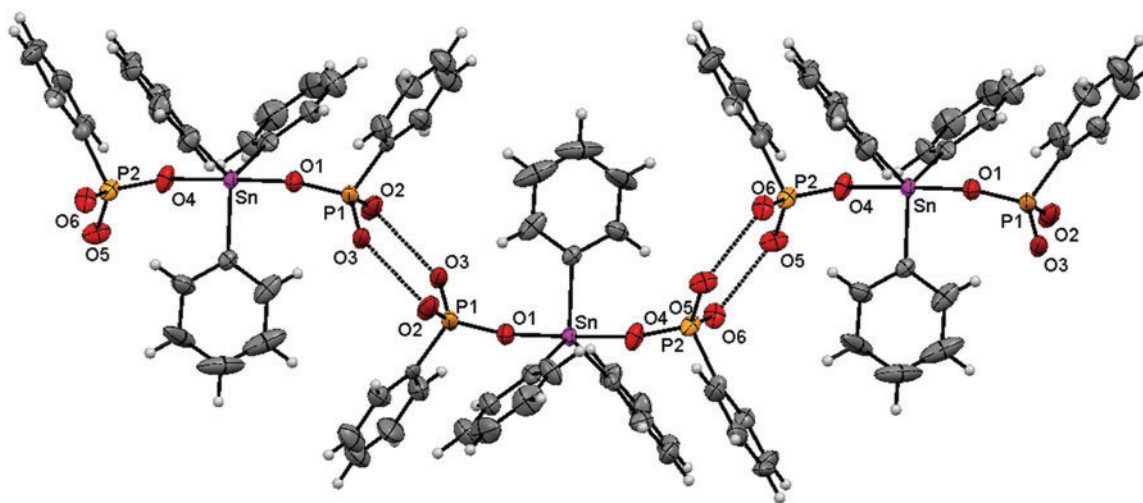


Figure 2 Infinite chain of $[(\text{PhPO}_3\text{H})_2\text{SnPh}_3]^-$ (H atoms are omitted for clarity).

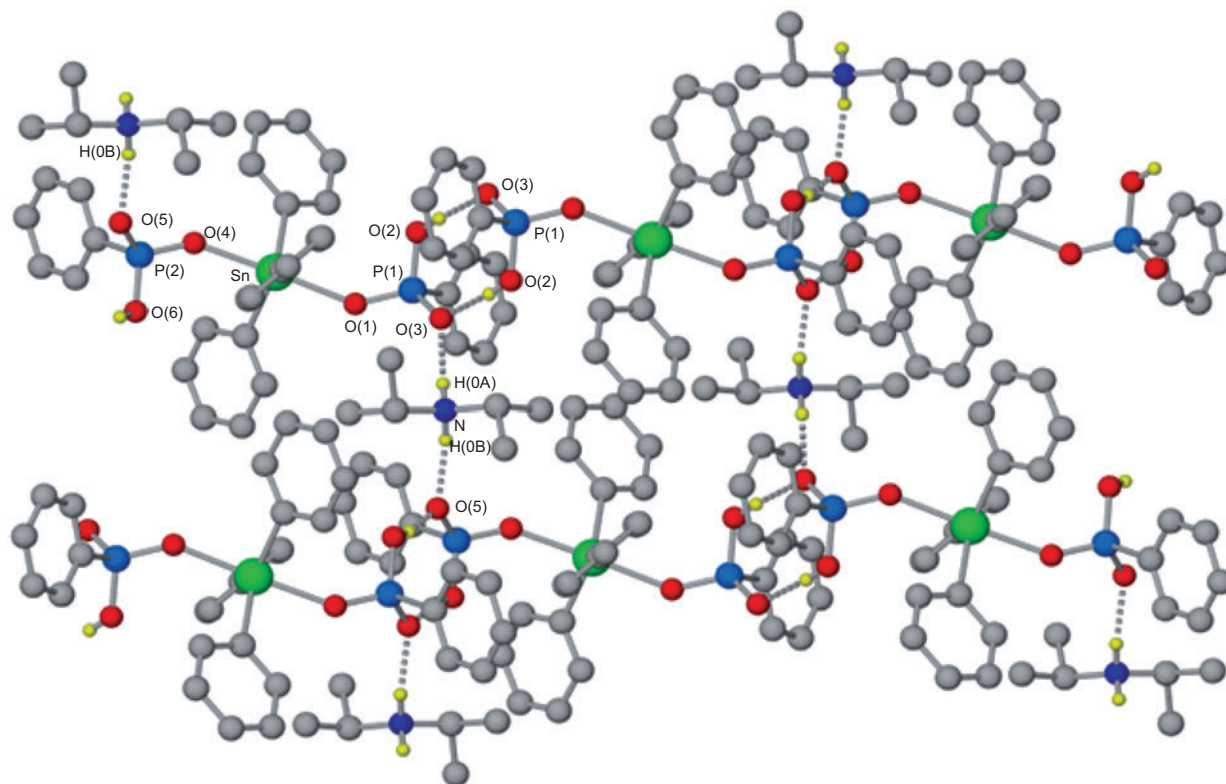


Figure 3 Three-dimensional structure of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$ showing the labelling scheme.

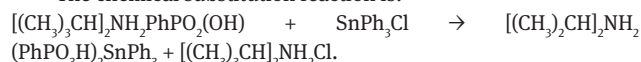
SnMe_4 , all set to 0.00 ppm. The Mössbauer spectrum was obtained as described previously (Bancroft and Platt, 1972). Mössbauer parameters are given in mm s^{-1} (abbreviations: QS, quadrupole splitting; IS, isomer shift; Γ , full width at half-height).

All the chemicals (Aldrich Chemical Company, Inc; product of Germany) were used without any further purification.

Synthesis of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$

The phenylphosphonate salt $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2\text{PhPO}_2(\text{OH})$ was obtained by mixing aqueous solutions of $[(\text{CH}_3)_2\text{CH}]_2\text{NH}$ (0.80 g, 6.32 mmol) and $\text{PhPO}_2(\text{OH})_2$ (1 g, 6.32 mmol). The title compound was obtained as white crystalline solid by reacting the phenylphosphonate salt (0.250 g, 0.870 mmol) with triphenyltin chloride (0.167 g, 0.435 mmol) in ethanol (yield 76%; 0.253 g; mp 177°C). After 96 h of slow evaporation of the solution, colourless crystals $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2(\text{PhPO}_3\text{H})_2\text{SnPh}_3$ suitable for X-ray structure determination were collected within the solvent. The powder obtained after complete solvent evaporation has the formula $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2\text{Cl}$ according to its infrared spectrum.

The chemical substitution reaction is:



Analytical data: [%Found (%calc. for $\text{C}_{36}\text{H}_{43}\text{NO}_6\text{P}_2\text{Sn}$)]: %C: 56.80 (56.42); %H: 5.22 (5.66); %N: 1.78(1.83). Infrared data (cm^{-1}): 3297 (vs) 3224 (s) νNH_2 ; 2854 br, 1280 s νOH ; 1174 s, 1112 s, 1062 vs. νPO_3 ; 947s νPC ; 506 w δPO_3 . Mössbauer data (mm s^{-1}): IS=1.24, QS=3.50, Γ =0.87. NMR data: [solvent: CDCl_3 ; $\delta(\text{ppm})$] ^1H NMR: 1.17 [s, 12H, CH_3 - $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2$]; 2.51 [s, 2H, $-(\text{CH})$ - $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2$]; 3.27

[s, 2H, $-\text{NH}_2$ - $[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2$]; 7.66 [complex pattern, 5H, PhPO_3H and 15H, SnPh_3]; 8.43 [s, 1H, OH]; ^{119}Sn : -237.

Structure determination

A crystal of approximate dimensions $0.25 \times 0.25 \times 0.20 \text{ mm}^3$ was used for data collection (Nonius Kappa CCD diffractometer). Data were collected at 150 K using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$); refinement was full-matrix least-squares based on F 2 , the absorption correction was semi-empirical from equivalents. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F 2 . Program(s) used to solve the structure: SIR97 (Altomare et al., 1999); program used to refine structure: SHELXL (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997, 1999). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 859694. Crystal data and structure refinement: empirical formula: $\text{C}_{36}\text{H}_{43}\text{NO}_6\text{P}_2\text{Sn}$; formula weight: 767.16; crystal system: triclinic; space group: $P \bar{1}$; a(\AA): 11.0654(3); b(\AA): 12.3229(4); c(\AA): 13.6187(3); α ($^\circ$): 105.168(2); β ($^\circ$): 95.366(2); γ ($^\circ$): 93.835(2); V(\AA^3): 1776.39(8); Z: 2; ρ_{calc} (mg m^{-3}): 1.425; $\mu(\text{Mo-}\text{K}_\alpha)$ (mm^{-1}): 0.854; F(000): 780; crystal size (mm^3): $0.25 \times 0.25 \times 0.20$; reflections collected: 36208; independent reflections: [R(int)] 8099 [0.0839]; reflections observed: ($>2\sigma$) 6956; absorption correction: semi-empirical from equivalents; max., min. transmission: 0.8478, 0.8149; refinement method: full-matrix least-squares on F 2 ; goodness-of-fit: 1.028; final R indices: [I $> 2\sigma$ (I)]=0.0838, 0.2665; R indices (all data): 0.1179, 0.2768; largest diff. peak and hole (e \AA^{-3}): 4.755, -1.899.

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